directions. In deriving (5), we have set equal to zero $J_{xz\,yz}$ and $J_{xy\,xy}$, the two antiferromagnetic parameters that dominate the picture in $[(en)_2Cr(OH)_2Cr(en)_2]Br_4{\cdot}2H_2O$[3] and $[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]Cl_4{\cdot}4H_2O$.[3] The two ferromagnetic parameters $J_{xz\,yz}$ and $J_{xz\,xy}$ have magnitudes similar to those in the systems studied in ref 3. With the parameters in (5) the total energy splitting of the $^2E_g{}^4A_{2g}$ final states is calculated as 50 cm^{-1}, in fair agreement with the experimentally observed spread of 31 cm^{-1} at 4.2 K. The calculated excited-state levels are shown in Figure 4 with the observed transitions (Figure 2) indicated schematically as arrows. An independent check of these parameter values is based on the relationship

$$J = {}^1\!/_9 \sum_{ij} J_{a_ib_j} \qquad (6)$$

We obtain the value J = 5 cm^{-1}, in exact agreement with the ground-state exchange parameter. This is reasonable because both $^4A_{2g}$ and ^2E_g are derived from the same electron configuration. We feel, therefore, that the above orbital parameters are meaningful, because they lead to a consistent picture not only for the title compound but also in comparison with other bis(μ-hydroxo)-bridged chromium(III) complexes.

Assignments of individual absorption bands to the $^2E_g{}^4A_{2g}$ dimer levels cannot be made with any confidence. We notice that the number of overlapping bands in the 14 400-cm^{-1} system exceeds the allowed (ΔS = 1) four at 4.2 K. Since all the intensity in this spectral range is probably due to electronic origins, there must be ΔS = 2 transitions contributing to the intensity. Weak ΔS = 2 transitions have also been observed in $[(en)_2Cr(OH)_2Cr(en)_2]Br_4{\cdot}2H_2O$.[3] Deviations from the theoretically assumed isotropy of the dimer levels are most likely to be responsible for this.

Acknowledgment. We thank K. Mattenberger for performing the susceptibility measurements. Financial support of this work by the Swiss National Science Foundation is acknowledged.

Registry No. $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4][(CH_3)_3C_6H_2SO_3]_4{\cdot}4H_2O$, 106402-71-5.

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Single-Crystal X-ray Structure of the High-Temperature Superconductor $Ba_2YCu_3O_{7-x}$

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Received July 2, 1987

We have determined the crystal structure of the high-temperature superconductor $Ba_2YCu_3O_{7-x}$ by single-crystal X-ray diffraction techniques. This material, which has a critical temperature of about 90 K, is orthorhombic with lattice parameters a = 3.829 (1), b = 3.886 (1), and c = 11.694 (3) Å, for space group *Pmmm*, Z = 1. The structure is a variant of the simple perovskite arrangement with an ordering of the Ba and Y cations. In the layers normal to the c axis there is a total absence of oxygen for those containing Y cations, while there is an oxygen vacancy and a partially occupied oxygen site in the Cu layer between the Ba layers. A specimen of apparent tetragonal symmetry was also studied, but the tetragonality, in that case, was the result of twinning of the orthorhombic structure.

Introduction

The structure of $Ba_2YCu_3O_{7-x}$ has been a matter of great interest and considerable discussion, since it was reported that this material exhibited superconductivity at approximately 90 K. The general picture of a layered variant of perovskite has been proposed by several investigators, although there seems to be some confusion regarding the details of the structure, especially the positions and occupancy of the oxygen sites. The high-resolution neutron powder diffraction work of Beno et al.[1] described an orthorhombic cell similar to that presented here. There have been other reports, however, of another orthorhombic cell[2] and of a tetragonal structure.[3] In this paper, we report two single-crystal studies: one is for the orthorhombic single crystal; the other deals with what appeared to be a tetragonal single crystal, but which we now believe to be a twinned orthorhombic crystal, with (110) as the twin plane.

Experimental Section

Reagent grade $BaCO_3$ (J. T. Baker), Y_2O_3 (Research Chemicals, 99.9% pure), and CuO, GR grade (EM Science, analyzed by H_2 reduction as 99.9% CuO), were weighed out in the 2:1:3 cation ratio. The mixture was wet-milled for 3 h in a polyethylene jar with dense ($^3/_8$ in. diameter) zirconia media in water containing a small amount of Triton X-100 wetting agent. The milled mixture was oven dried at 120 °C overnight. The dried material was reacted by heating at 100 °C/h to 950 °C and holding for 24 h, followed by furnace cooling at <150 °C/h to room temperature. The reaction was carried out in an ambient air atmosphere with the powder bed less than a centimeter in depth. The product was gently crushed in a porcelain mortar and pestle. Small irregularly shaped single crystals were identified and isolated in a sample of this black material.

Table I. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for the Tetragonal Crystal in $P\bar{4}2m$

atom	x	y	z	$U_{equiv}{}^a$	occupancy
Cu(1)	0	0	0	23 (1)	1.00
Cu(2)	0	0	3556 (2)	21 (1)	1.00
Y	5000	5000	5000	20 (1)	1.00
Ba	5000	5000	1849 (1)	22 (1)	1.00
O(1)	5000	0	0	28 (8)	0.40
O(2)	0	0	1538 (7)	29 (2)	1.00
O(3)	5000	0	3782 (5)	20 (2)	1.00

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

For both structures, single-crystal data were collected by using a Nicolet P3F automated single-crystal diffractometer and monochromatized Mo Kα radiation (λ = 0.710 69 Å) at room temperature. An $\omega/2\theta$ scan was used to collect an entire sphere of data ($\pm h,\pm k,\pm l$) from 4 to 50° in 2θ. Since the crystals were very irregular, indices could not be assigned to the faces. Therefore, an empirical absorption correction was applied to the data for each crystal (μ = 293.4 cm^{-1}; μr = 2.0). The materials were known to be perovskites, and therefore, atomic positions were assigned based on this structure and refined by using the SHELXTL program package.[4] All atoms were treated as anisotropic, and the occupancies of the oxygen atoms were allowed to refine. The function minimized in least-squares refinement is $\sum w(|F_o| - |F_c|)^2$. $R = \sum ||F_o| - |F_c||/\sum|F_o|$.

Powder diffraction data were collected by using a Siemens D500 automated diffractometer using Cu Kα radiation. Powder patterns were

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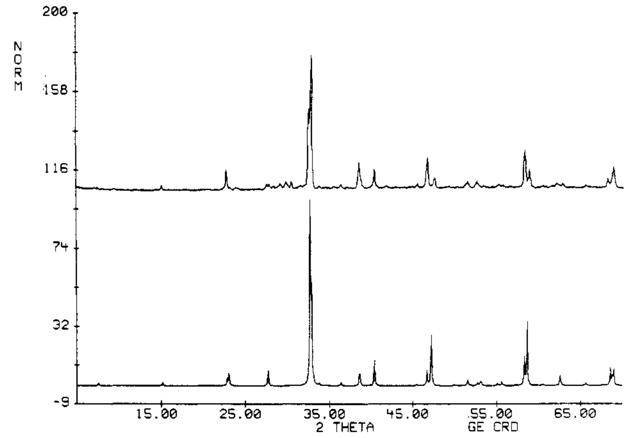

Figure 1. Upper: experimental powder pattern from $Ba_2YCu_3O_{7-x}$. Lower: simulated pattern from the "tetragonal" crystal structure.

simulated by using the POWD7 program.[5]

The "Tetragonal" Structure

Data were collected on an irregular crystal (120 × 140 × 100 μm) that exhibited tetragonal lattice constants $a = 3.854$ (2) and $c = 11.687$ (6) Å. A total of 2366 reflections were collected: 377 unique and 371 observed with $F > 3\sigma(F)$ and $R_{merge} = 0.0711$. The data contained no systematic absences, and therefore, the space group was not uniquely determined. $P\bar{4}2m$ and $P\bar{4}m2$ were evaluated based upon prior work in the literature.[3] The structure refines acceptably in either space group. $P4/mmm$ is also a possible space group, and although refinement in this space group was not attempted, we are confident that results similar to those described here could be obtained. The coordinates obtained for $P\bar{4}2m$ are listed in Table I and represent a refinement with $R = 0.0762$ for 26 parameters. In addition, because of the possibility of orthorhombic symmetry, the space group *Pmmm* was tried with this set of data, and similar atomic positions and occupancies were obtained.

The structure contains layers of Y atoms with no oxygen atoms, layers of Ba atoms with fully occupied oxygen positions, layers of Cu atoms between the Y and Ba layers containing fully occupied oxygen positions, and layers of Cu atoms between the Ba layers that contain 40% occupied oxygen positions.

When the powder pattern was simulated from these coordinates, major discrepancies between the simulated and experimental patterns were observed. In Figure 1, one can see that the doublet intensities of the lines at approximately 32.0, 47, and 58° in 2θ are reversed, and no reasonable explanation (i.e., preferred orientation) could be found. A further evaluation of the diffraction intensity profiles obtained from the crystal indicated some asymmetry. We interpret this to be a subtle twinning of the crystal caused by a 90° rotation about the c axis.

The Orthorhombic Structure

The twinning hypothesis was given more validity by the study of a second crystal, much smaller than the first (70 × 60 × 50 μm), which was isolated from the same preparation. This crystal exhibited orthorhombic lattice parameters $a = 3.830$ (1), $b = 3.886$ (1), $c = 11.707$ (4) Å. A total of 2062 reflections were collected; 347 unique and 327 observed with $F > 3\sigma(F)$ and $R_{merge} = 0.0448$. Data collected on this crystal refined in *Pmmm* with coordinates similar to those obtained by Beno et al. (see Table II). The only difference between this structure and the "tetragonal" crystal is that the oxygen vacancies in the Cu layers between the Ba layers are ordered instead of statistically distributed between the sites. The oxygen disorder observed with the "tetragonal" structure is consistent with a picture of twinning along the {110} plane. In addition, the a lattice constant of the "tetragonal" crystal is the average of the a and b lattice constants of the orthorhombic crystal, with the c lattice constant almost identical.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for the Orthorhombic Crystal in *Pmmm*

atom	x	y	z	U_{equiv}[a]	occupancy
Cu(1)	0	0	0	21 (1)	1.00
Cu(2)	0	0	3557 (2)	17 (1)	1.00
Y	5000	5000	5000	17 (1)	1.00
Ba	5000	5000	1846 (1)	19 (1)	1.00
O(1)	0	5000	0	28 (8)	0.72
O(2)	0	0	1550 (12)	26 (4)	1.00
O(3)	0	5000	3775 (10)	14 (3)	1.00
O(4)	5000	0	3780 (11)	17 (3)	1.00

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Lengths (Å) for the Orthorhombic Crystal

Y–O(3)	2.392 (7)	Y–O(4)	2.412 (8)
Ba–O(1)	2.888 (3)	Ba–O(2)	2.750 (3)
Ba–O(3)	2.961 (9)	Ba–O(4)	2.983 (10)
Cu(1)–O(1)	1.943 (2)	Cu(1)–O(2)	1.815 (14)
Cu(2)–O(2)	2.350 (14)	Cu(2)–O(3)	1.960 (2)
Cu(2)–O(4)	1.933 (3)		

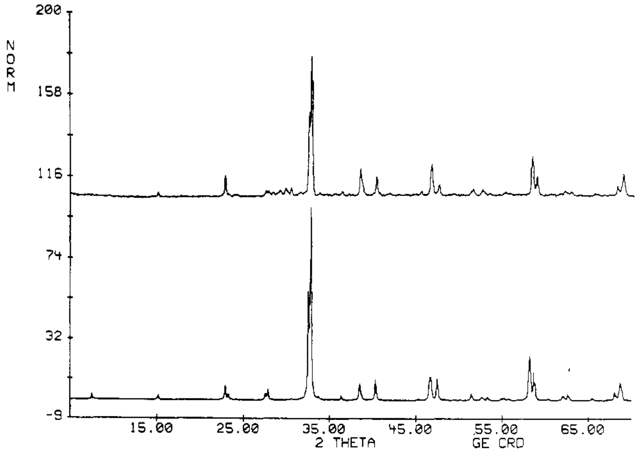

Figure 2. Upper: experimental powder pattern from $Ba_2YCu_3O_{7-x}$. Lower: simulated pattern from the orthorhombic crystal structure.

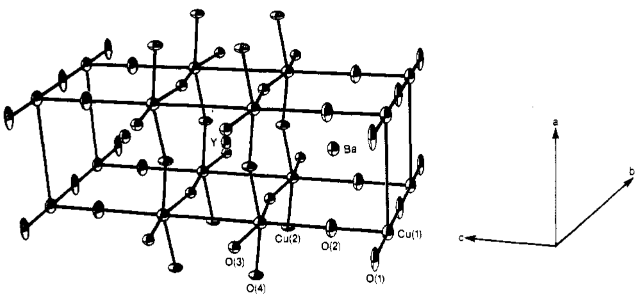

Figure 3. Thermal ellipsoid (50%) plot of the orthorhombic crystal structure of $Ba_2YCu_3O_{7-x}$.

The simulated powder pattern of the orthorhombic structure is a much better match to the experimental pattern than the "tetragonal" structure (see Figure 2). Coordinates for this structure can be found in Table II, with anisotropic thermal parameters listed in the supplementary material. Selected bond lengths can be found in Table III, and a plot of the structure is given in Figure 3. This refinement resulted in $R = 0.0521$ for 31 parameters.

Discussion

The twinning in the microstructure of this material has been observed by other workers[6] as well as in this laboratory.[7] With the slight difference in a and b dimensions and the fact that cation

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positions and some oxygen positions are maintained in a rotation of 90° about the *c* axis, the twinning results only in a difference in the remaining oxygen distribution, producing a random instead of an ordered arrangement. While a truly tetragonal phase may exist, our results suggest that it is very easy to identify a twinned orthorhombic crystal as this tetragonal phase.

It is grafitying that our minute crystal is representative of the bulk polycrystalline specimen. We have found the powder pattern simulation to be a valuable adjunct to the single-crystal study.

Although our results support the structure proposed by the neutron diffraction study, there are some important differences in the occupancies of the oxygen sites. In this study three of the four oxygen positions are fully occupied, with the fourth, O(1), only 72% occupied. In the neutron diffraction study two oxygen sites were partially occupied: O(1) at 92% and O(4) at 95%. This may point out the importance that sample history has on the distribution of oxygen in such materials, without significantly affecting the stoichiometry. The composition of our material is $Ba_2YCu_3O_{6.7}$ compared to $Ba_2YCu_3O_{6.81}$ from the neutron data. The unusual thermal parameters obtained for the partially occupied oxygen positions in both this X-ray study and the neutron structure should be noted. This is the only site in the structure where there seems to be substantial anisotropy in the thermal motions, with the biggest deviations along the *a* axis, toward the unoccupied oxygen site.

The existence of both Cu^{3+} and Cu^{2+} in this material can be deduced from the stoichiometry of the material and a consideration of the charge balance. Since it has been proposed that this influences the high-temperature superconductivity of the material,[8] we have examined the observed electron density about the copper sites in order to try to verify the existence of the two oxidation states of the Cu. There is a 10% lower integrated density about Cu(1) than Cu(2). Cu(2) has a more regular square-planar arrangement of oxygens, with a fifth long bond of 2.350 (14) Å, and thus appears to be similar to a common Cu^{2+} configuration. The arrangement of the four oxygen atoms about Cu(1) is distorted, involving short Cu(1)–O(2) distances of 1.815 (14) Å. This, combined with the lower electron density, is suggestive that the Cu(1) site might contain at least a partial occupancy by Cu^{3+}.

Supplementary Material Available: Table SI of anisotropic thermal parameters for the orthorhombic structure (1 page); tables of observed and calculated structure factors for both structures (2 pages). Ordering information is given on any current masthead page.

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Studies on the Low-Temperature Synthesis and Surface Chemistry of Iron Monoxide

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Received November 17, 1986

Thin films of FeO have been made by the action of steam on iron foils or flat coupons at temperatures between 540 and 800 °C. Growth rates at 800 °C are quite high, about 20 μm/h. We have found that the time of treatment for any given thickness is critical, at constant temperature and flow rates of steam. For example, a foil of thickness 127 μm was essentially all converted to FeO by a 3-h treatment at 800 °C. At longer time, the outside of the foil begins to convert to Fe_3O_4, and at still longer times, the sample becomes entirely Fe_3O_4. The effect of added oxygen has been studied, and it has been found that the amount of oxygen normally dissolved in water presents no problem. However, higher amounts of oxygen, while increasing the growth rates of the FeO, also produce some Fe_2O_3. Iron monoxide is an active catalyst for the formation of filamentous carbon (from hydrocarbons at 700 °C), being at least 1 order of magnitude more active than iron and nickel foils at these temperatures. The basis for this high activity has been investigated and is probably due to the fact that FeO very rapidly reduces to porous iron while the coking is occurring, which must then be of correct porosity to form carbon filaments in profusion.

Introduction

Although there has been extensive publication on the formation and synthesis of the oxides of iron,[1–14] little work has been done on the synthesis of ferrous oxide (iron monoxide, FeO, Wüstite) from metallic iron at temperatures below 1000 °C.

We have found that it is possible to synthesize FeO starting from either pure iron foils or from mild steel by the action of steam alone at temperatures above 540 °C. At the lower temperatures (580–650 °C) the reaction rate was very low, resulting in very small weight gains, so identification of the product of the reactions was done by Auger analysis.[15] At higher temperatures, for example 800 °C, we found it possible to convert all of a 0.005-in. iron foil into FeO by a short steam treatment. In addition, we have shown by X-ray measurements that after all the metallic iron had been converted to FeO, continuing steam treatment began transforming the outside of the FeO to Fe_3O_4. Longer treatments converted all of the FeO to pure Fe_3O_4, as shown by weight changes and confirmed by X-ray analysis.

Out interest in FeO was aroused by its very high efficiency as a catalyst for the production of filamentous carbon,[16] and a patent

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